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(54) Title: A WIPER CONTAINING A CONTROLLED-RELEASE ANTI-MICROBIAL AGENT

(57) Abstract: A wiper having a controlled release anti-microbial agent therein for providing anti-microbial cleansing of surfaces is provided. The wiper is formed from an absorbent base web to which an anti-microbial formulation is adhered. The formulation includes an anti-microbial agent that is capable of being controllably released from the wiper. In some embodiments, a polymer mixture may be employed to control the rate of release of the anti-microbial agent. Various anti-microbial agents, such as metal ions and organic compounds may be employed.



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A WIPER CONTAINING A CONTROLLED-RELEASE ANTI-MICROBIAL AGENT

The present invention is based on provisional patent application Serial Number 60/173,400 filed December 28, 1999, and
5 priority is hereby claimed therefrom.

Field of the Invention

The present invention generally relates to a wiper, such as the type used to disinfect hard surfaces in food service and medical applications. More particularly, the present invention is directed to a
10 wiper having an anti-microbial agent such that it can be controllably released over an extended period of time.

Background of the Invention

Microbial contamination can have a detrimental effect on any item ordinarily used by consumers or merchants, particularly items
15 used in the medical and food service industries. For example, due to various bacterial outbreaks, there have been at least 200 food poisoning deaths reported in the last 10 years. Moreover, more Americans die from hospital infections each year than from car accidents and homicides combined.

20 Much of this contamination occurs due to the migration of microorganisms from hard surfaces such as table tops and counter tops to food and to food handlers, thence to food. For example, in the food service industry, contamination commonly occurs on stainless steel surfaces used for food preparation. Various food products are
25 prepared on hard surfaces such as counters, tables, and the like. Bacteria from these products will often collect on such surfaces and, if the surface is not cleansed regularly, can transfer from product to product or from product to the preparer. Numerous studies indicate that cross-contamination occurs as a result of a microorganism
30 coming in contact with a person's hands or with a cleaning cloth and

thereafter contaminating other items touched by the cloth or hands, such as equipment or other surfaces.

As a result, wipers that contain anti-microbial agents have been employed to prevent such surface and cloth contamination.

5 Currently, most of these anti-microbial wipers are impregnated with anti-microbial agents that are delivered to the user in a pre-moistened form. However, the disinfecting agent within the wiper can be readily exhausted after only a few washings and rinsings to remove dirt after a period of use. Thus, it is believed that such pre-moistened wipers
10 either inhibit growth on the wipers and/or the hard surfaces cleaned only mildly or may only be used for a limited number of wipes.

Some anti-microbial wipers have been developed that are not pre-moistened. For example, one such anti-microbial wiper that can be delivered in a dry condition is disclosed in U.S. Patent No.
15 5,213,884 to Fellows. In the Fellows patent, a wiper is disclosed that contains a hot melt adhesive powder mixed with a chlorine release agent. The adhesive powder and chlorine release agents are incorporated into a tissue suitable for use in the disinfection of hard surfaces.

20 Although the wiper disclosed by Fellows can be delivered in a dry form, it apparently fails to provide sufficient disinfection over an extended period of time -- similar to pre-moistened wipers. After being contacted with water, the release of the anti-microbial agent in such wipers capable of being delivered in a dry state occurs readily
25 without control. This prevents the wiper from sustaining its anti-microbial activity after repeated washings and rinsings.

Another anti-microbial wiper has been marketed by Pal International, Inc. of England under the name WIPEX®. According to the sales literature, this wiper contains poly(hexamethylenebiguanide
30 hydrochloride), alkyldimethylbenzyl ammonium chloride, and the disodium salt of ethylenediaminetetraacetic acid (E.D.T.A.). In

addition, the wipers include indicator stripes that are stated to fade gradually as the disinfectants are depleted from the wiper. It is believed that U.S. Patent No. 4,311,479 to Fenn *et al.* is related to this particular anti-microbial cloth. It is believed, however, that these wipers have not proven to be very effective in reducing certain bacterial activity. Also, it is believed that they might retain only limited anti-microbial activity after several rinses.

In U.S. Patent No. 4,906,464, Yamamoto *et al.* describe the preparation of a dispersion of an antibiotic powder, such as a zeolite or an amorphous aluminosilicate whose ion exchange ions have been partially or completely ion-exchanged with antibiotic metal ions and/or ammonium, in a dispersion medium, such as a thermoplastic resin, a polyol, an alcohol, a higher alcohol, a higher fatty acid, or a resin emulsion. The components are mixed at a reduced pressure and at a temperature at which the dispersion medium is a liquid, and where the viscosity of the dispersion is between 2,000 cp. to 200,000 cp. Such dispersions were applied to the surface of nylon, rayon and cotton cloths, and it was shown that the treated cloths apparently had the capacity to kill bacteria within 24 hours in solutions that were sprayed onto the treated cloths. A principal object of the invention was to provide a method for uniformly dispersing antibiotic powder in a dispersing medium such as a resin.

In U.S. Patent No. 4,938,958, to Niira *et al.*, an antibiotic resin composition was described as including a resin and an antibiotic zeolite in an amount of from 0.05% to 80% by weight of the composition, where the zeolite contained from 0.1% to 15% by weight of silver and from 0.5% to 15% by weight of ammonium ions. In U.S. Patent No. 4,938,955, a group from the same assignee disclosed an antibiotic resin composition that included a resin, an antibiotic zeolite like the one just described, and a discoloration inhibitor. An object of the invention was to provide an antibiotic resin composition which

does not discolor with time and which exhibits excellent antibiotic effect.

The same type of antibiotic zeolite was incorporated into a transparent self-supporting antibiotic film (U.S. Patent No. 5,556,699).
5 The film was of an organic polymer and was not over 10 microns in thickness, and included 25 to 100 mg of the antibiotic zeolite per square meter. It was stated that the antibiotic activity was fully effective and complete (100%). An object of the invention was to provide an antibiotic zeolite-containing film having a relatively low
10 content of antibiotic zeolite, which exhibits a satisfactory antibiotic action and is also transparent. Applications were included that showed the lamination of the film to a substrate, such as a resin film, and it was suggested that the laminated film could further be laminated to a layer of resin, metal, or paper to form sheets or other
15 molded products. The molding of such a laminated film to a toothbrush was demonstrated.

In U.S. Patent No. 4,615,937, to Bouchette, an antimicrobially active wet wiper is described that comprises bonded fibers of a nonwoven web, which are bonded together by a uniformly distributed
20 binder. An antimicrobial agent is bound to the fibers and the binder in a manner that prevents the agent from substantively diffusing from the fibers or the binder, whether the wiper is wet or dry. A purpose of the invention is to prevent the transfer of the anti-microbial agent to a user's skin, where it might leave an irritating residue. Apparently,
25 therefore, any liquid that would be left by the wiper on a wiped surface would be substantially free of the anti-microbial agent.

Thus, it remains that a need currently exists for a more effective wiper that disinfects hard surfaces and inhibits cross-contamination. In particular, a need exists for a wiper that contains an anti-microbial
30 agent that is slowly released when contacted by water, thereby allowing the wiper to provide an anti-microbial solution and to sustain

its anti-microbial effectiveness after repeated washing and rinsing operations.

Summary of the Invention

Accordingly, an object of the present invention is to provide a wiper suitable for use in disinfecting hard surfaces.

It is another object of the present invention to provide a wiper containing an anti-microbial agent that can remain effective after repeated washing and rinsing.

Still another object of the present invention to provide a wiper containing an anti-microbial agent that can remain effective after repeated washing and rinsing by releasing the anti-microbial agent at a controlled rate.

It is another object of the present invention to provide a wiper in which the cloth-like base web is applied with a formulation containing an anti-microbial agent.

Another object of the present invention is to provide a formulation that contains an anti-microbial agent and a polymer.

It is another object of the present invention to provide a formulation that contains an anti-microbial agent and a polymer that can retain its strength and adhesion properties after being applied to the base web, and thereafter creped and cured.

These and other objects of the present invention are achieved by providing a wiper capable of providing liquid anti-microbial solution after numerous rinse cycles. The wiper generally includes a controlled release anti-microbial formulation comprising an anti-microbial agent, which formulation is adhered to an absorbent, cloth-like web which retains liquid after each rinse cycle. The combination of the anti-microbial formulation and the retained liquid in the wiper is adapted so that the formulation releases sufficient anti-microbial agent into the retained liquid after each of at least five normal rinse cycles so that the retained liquid is an anti-microbial solution. In

certain embodiments, the anti-microbial formulation can include an anti-microbial agent encapsulated in, adsorbed to, or as a part of a particle or microcapsule. In certain embodiments, the anti-microbial formulation may be in the form of an anti-microbial agent that is
5 coated by or enclosed in a polymer coating.

In accordance with the present invention, any material commonly used in the art to manufacture cloths, such as wipers, can be used as the base web. In particular, a base web of the present invention is typically made from a nonwoven polymeric or paper-based web. More particularly, a base web of the present invention
10 can be made from pulp fibers, synthetic fibers, thermomechanical pulp, or mixtures thereof such that the web has cloth-like properties. For instance, the base web can be made from softwood pulp fibers, such as Northern softwood Kraft fibers, redwood fibers and pine
15 fibers. Moreover, the base web can also include staple fibers, such as polyolefin fibers, polyester fibers, nylon fibers, polyvinyl acetate fibers, cotton fibers, rayon fibers, non-woody plant fibers, and mixtures thereof.

A wiper of the present invention also includes an anti-microbial formulation that can be adhered to the base web. In accordance with
20 the present invention, the formulation can contain an anti-microbial agent that is adapted to being released from the anti-microbial formulation at a controlled rate. In general, an anti-microbial agent of the present invention can be made from any additive that can be used
25 as a disinfectant in wipers.

As stated, an anti-microbial formulation of the present invention may also comprise a polymer or polymer mixture that can aid in binding the anti-microbial agent to the fibers and controlling the release of the anti-microbial agent from the wiper. Although not
30 required, the polymer(s) in the polymer mixture can, in some embodiments, be capable of swelling in water. In general, any such

water-swellaable polymer is suitable for use in the present invention. Examples of water swellaable polymers that can be used in the present invention include adhesives such as acrylates, styrene butadiene, vinyl chlorides, methacrylates, acrylics (such as carboxylated
5 acrylics), and vinyl acetates (such as self cross-linking ethyl vinyl acetate, hydrolyzed polyvinyl acetate, or non-cross-linking ethyl vinyl acetate). In some particular embodiments, the water-swellaable polymer can comprise carboxylated acrylics.

10 In certain embodiments of the present invention, a polymer mixture may also comprise a polymer that can become cross-linked when dried. The use of cross-linkable polymers, such as latex adhesives, can allow the release of the anti-microbial agent to be further controlled. Specifically, increasing the amount of cross-linking in the adhesive can result in less swelling, which in turn results in a
15 faster release of the anti-microbial agent when the wiper is contacted with water.

In accordance with the present invention, other various components can also be added to the polymer mixture of the anti-microbial formulation as desired. For example, plasticizers, such as
20 glucose triacetate, can be added to the polymer mixture to aid in the migration of the anti-microbial agent to the polymer surface. In addition to plasticizers, cross-linking agents, catalysts, thickeners, defoamers, colorants, water, etc., can also be added to an anti-microbial formulation of the present invention. Furthermore,
25 chemicals such as stabilizers, viscosity modifiers, composite particles, or surfactants, can be added as well.

In some embodiments, a visual sensor, colorant, or dye can be incorporated into the subject wiper to indicate when the anti-microbial agent has been exhausted. For example, sodium thiosulfate and
30 various blue dye mechanisms, such as those employed in the WIPEX® wipes may also be employed. Furthermore, a visual sensor

mechanism disclosed in co-pending and co-owned U.S. Provisional Application entitled "Use-Dependent Indicator System for Absorbent Articles", which is incorporated herein by reference thereto, can also be utilized in conjunction with a wiper of the present invention.

5 According to the present invention, the release rate of the anti-microbial agent from the anti-microbial formulation can generally be controlled in a variety of ways. In one embodiment, for example, the release rate of the anti-microbial agent can be controlled by the incorporation of the anti-microbial agent as a part of a system that
10 provides controlled release properties. For instance, certain anti-microbial agents, such as silver can be included as an ion that is bound by an ion exchange resin, such as a zeolite. Such systems can be supplied in the form of powders and are adapted to release the anti-microbial agent -- silver ions, in this case, from a wiper at a
15 controlled rate. Moreover, other mechanisms that can aid in controlling the release rate of the anti-microbial agent include varying the size of solid anti-microbial agent particles, the use of polymerization chemistries, the employment of at least partially encapsulated solid anti-microbial particles, the use of porous
20 absorbents, the use of soluble binders, or combinations thereof.

 An alternative to providing the anti-microbial agent as part of a system that has controlled release properties, is the provision of a formulation in which the release of the anti-microbial agent from the wiper can also be controlled by an anti-microbial agent that is
25 contained within, or in a mixture with a polymer or polymer mixture. In particular, the components of the polymer mixture can be selected and varied to control the release of the anti-microbial agent without adversely affecting the strength and adhesion properties of the polymer mixture. For example, the release rate of the anti-microbial
30 agent can be controlled by varying the type and amount of polymer,

cross-linking agent, plasticizer, etc., used in a polymer mixture of the present invention.

Furthermore, in some embodiments, the method of applying a formulation of the present invention to the base web can also aid in controlling the release of the anti-microbial agent. Generally, a formulation of the present invention can be applied to the base web by any method of application, including, but not limited to, print, print crepe, spray, blade, saturant, coating, droplet throw, and foam application methods. For example, in one embodiment, the formulation can be applied to at least one side of the base web. In certain embodiments, the formulation may be applied to both sides of the base web.

In one embodiment, the formulation can be applied onto the base web in a pre-selected pattern using a print roll. The pre-selected pattern used to apply the formulation can be, in one embodiment, a reticular interconnected design. Alternatively, the pre-selected pattern can comprise a succession of discrete shapes, such as dots. In a further alternative embodiment of the present invention, the pre-selected pattern can be a combination of a reticular interconnected design and a succession of discrete shapes.

The formulation can also, in some embodiments, be applied to the base web such that it covers less than 100%, and more particularly from about 10% to about 60% of the surface area of each side of the web. Moreover, in some embodiments, the formulation can be applied to each side of the base web in an amount of up to about 2% to about 8% by weight of the web. Once applied, the formulation can penetrate the base web in an amount from about 10% to about 60% of the total thickness of the web.

In some embodiments, after applying the formulation to the base web, the web can then be creped to increase the softness, absorbency, and bulk of the web. Depending on the application, one

or both sides of the web can be creped. Furthermore, the base web can be dried and cured after applying the formulation and creping, if necessary. Curing can increase the strength of the base web, as well as aid in controlling the release time of the anti-microbial agent. In one embodiment, for example, controlling the degree of polymer curing can enhance the control over the amount of swelling by a polymer when the wiper is contacted with water. This, in turn, may provide control over the release rate of the anti-microbial agent.

Other objects, features and aspects of the present invention are discussed in greater detail below.

Detailed Description of Representative Embodiments

Reference now will be made in detail to the embodiments of the invention, one or more examples of which are set forth below. Each example is provided by way of explanation of the invention, not limitation of the invention. In fact, it will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. For instance, features illustrated or described as part of one embodiment, can be used on another embodiment to yield a still further embodiment. Thus, it is intended that the present invention cover such modifications and variations as come within the scope of the appended claims and their equivalents. Other objects, features and aspects of the present invention are disclosed in or are obvious from the following detailed description. It is to be understood by one of ordinary skill in the art that the present discussion is a description of exemplary embodiments only, and is not intended as limiting the broader aspects of the present invention.

In general, the present invention is directed to a wiper containing an anti-microbial agent that is incorporated into an anti-microbial formulation that is applied to a base web such that the anti-microbial agent can be released from the anti-microbial formulation at

a controlled rate until the anti-microbial agent is exhausted. When the subject wiper is contacted with water, a certain amount of water is absorbed by the absorbent web and, when the wiper is wrung out, or permitted to drip until excess water has been lost, the absorbent web retains a certain amount of liquid. It has been discovered that by incorporating an anti-microbial agent within a formulation that is adhered to the web, the anti-microbial agent can be released at a controlled rate to bring the content of the anti-microbial agent in the retained liquid to a level where the retained liquid can act as an anti-microbial solution. Sufficient anti-microbial agent can be incorporated into the anti-microbial formulation and a sufficient amount of the formulation can be adhered to the web, so that only a part of the anti-microbial agent is released from the formulation during each normal rinse cycle and the wiper can continue to provide the retained liquid as an anti-microbial solution after multiple rinsing cycles.

An advantage of the subject wiper is that stronger anti-microbial agents can be employed than if such agents were used directly and not as a part of the subject anti-microbial formulation, and multiple washing and rinsing cycles can be realized without completely and quickly depleting the anti-microbial qualities of the wiper.

As used herein, the terms "anti-microbial agent" refers to a material that is capable of killing or reducing the growth rate of common disease causing bacteria.

The terms "anti-microbial solution", as used herein, refer to a liquid having in solution an amount of an anti-microbial agent that is sufficient to kill or reduce the growth rate of strains of common disease causing bacteria as compared with the same liquid without that amount of anti-microbial agent. In some embodiments of this invention, it is possible for the anti-microbial solution to act as a sanitizer solution or a disinfectant solution.

As used herein, the terms "anti-microbial formulation" refer to a combination of an anti-microbial agent and a material that serves to modulate the release rate of the agent when it is in contact with a liquid. The formulation, in some instances, can also adhere the agent to the web. When it is said that a material "modulates the release rate of the agent", or provides a "controlled release" feature, it is meant that the material reduces the rate of release of the agent into a liquid from what the rate would be if no such material were present.

As used herein, the terms "rinse cycle" and "washing and rinsing", mean the same thing and refer to the steps of contacting a wiper with water, followed by free drip and then by wringing or squeezing. A "normal rinse cycle", as those terms are used herein, refers to a manual rinse of the wiper with water, followed by hand wringing, as would typically occur under normal use conditions.

The terms "residual liquid", as used herein, refer to the liquid that is retained in a wiper after a rinse cycle.

In accordance with the present invention, an anti-microbial surface wiper is provided that contains a base web to which is adhered an anti-microbial formulation. In particular, an anti-microbial formulation of the present invention contains an anti-microbial agent that can be released at a controlled rate.

The process of forming a wiper made according to the present invention involves first forming a base web material. A base web of the present invention can generally be made from any absorbent material used in the art for wipers. In particular, any nonwoven polymeric or paper-based, generally absorbent, web is suitable for use in the present invention. Examples include webs made from pulp fibers, synthetic fibers, and mixtures thereof such that the web has cloth-like properties. In addition, the web can be a co-form material such as disclosed in U.S. Patent Nos. 4,100,324 to Anderson et al. and 5,350,624 to Georger et al., which are incorporated herein in their

entireties by reference thereto. The wipers may be packaged and made according to the disclosures of U.S. Patent Nos. 4,833,003 and 4,853,281 to Win et al.

5 For example, the material used to make a cloth-like base web of the present invention can include pulp fibers either alone or in combination with other types of fibers. The pulp fibers used in forming the base web may be softwood fibers having an average fiber length of greater than 1 mm and particularly from about 2 to 5 mm based on a length-weighted average. Such fibers can include
10 Northern softwood Kraft fibers, redwood fibers and pine fibers. Secondary fibers obtained from recycled materials may also be used.

In one embodiment, synthetic fibers, such as staple fibers (and filaments) can be also added to increase the strength, bulk, softness and smoothness of the base web. Staple fibers can include, for
15 instance, polyolefin fibers, polyester fibers, nylon fibers, polyvinyl acetate fibers, cotton fibers, rayon fibers, non-woody plant fibers, and mixtures thereof. In general, staple fibers are typically longer than pulp fibers. For instance, staple fibers typically have fiber lengths of 5 mm and greater.

20 The staple fibers added to the base web can also include bicomponent fibers. Bicomponent fibers are fibers that can contain two materials such as, but not limited to, two materials in a side-by-side arrangement or in a core and sheath arrangement. In a core and sheath fiber, the sheath polymer will usually have a lower melting
25 temperature than the core polymer. For instance, the core polymer, in one embodiment, can be nylon or a polyester, while the sheath polymer can be a polyolefin such as polyethylene or polypropylene. Such commercially available bicomponent fibers include CELBOND® fibers marketed by the Hoechst Celanese Company.

30 The staple fibers used in a base web of the present invention could also be curled or crimped. The fibers can be curled or crimped,

for instance, by adding a chemical agent to the fibers or subjecting the fibers to a mechanical process. Curled or crimped fibers may create more entanglement and void volume within the web and further increase the amount of fibers oriented in the -Z direction as well as increase web strength properties.

In general, base webs made according to the present invention can be made exclusively from synthetic fibers, such as fibers made from various polymeric materials. The synthetic fibers can be staple fibers or other various types of fibers or filaments. As described above, a base web of the present invention can also be made from a mixture of synthetic fibers and pulp fibers.

In one embodiment, when forming an anti-microbial wiper containing pulp fibers, the staple fibers can be added to the base web in an amount from about 5% to about 30% by weight and particularly from about 10% to about 20% by weight. For example, short staple fibers made from a polyester or polyolefin can be added to the base web. The fibers can have a length of from about $\frac{1}{4}$ of an inch to about 1 inch. The fibers can be mixed homogeneously with the pulp fibers in forming the web. Staple fibers can increase the strength and softness of the final product.

Besides pulp fibers and spunbonded fibers, thermomechanical pulp fibers can also be added to the base web. Thermomechanical pulp, as is known to one skilled in the art, refers to pulp that is not cooked during the pulping process to the same extent as conventional pulps. Thermomechanical pulp tends to contain stiff fibers and has higher levels of lignin. Thermomechanical pulp can be added to the base web of the present invention in order to create an open pore structure, thus increasing bulk and absorbency and improving resistance to wet collapse.

When present, the thermomechanical pulp can be added to the base web in an amount of from about 10% to about 30% by weight.

When using thermomechanical pulp, a wetting agent may also be added during formation of the web. The wetting agent can be added in an amount less than about 1% and, in one embodiment, can be a sulphonated glycol.

5 The fiber furnish used to form the base web can also be treated with a chemical debonding agent to reduce inner fiber-to-fiber strength. Suitable debonding agents that may be used in the present invention when the base web contains pulp fibers include cationic
10 debonding agents such as fatty dialkyl quaternary amine salts, mono fatty alkyl tertiary amine salts, primary amine salts, imidazoline quaternary salts, and unsaturated fatty alkyl amine salts. Other suitable debonding agents are disclosed in U.S. Patent No. 5,529,665 to Kaun, which is incorporated herein in its entirety by reference thereto.

15 In certain embodiments, the debonding agent can be an organic quaternary ammonium chloride. In these embodiments, the debonding agent can be added to the fiber slurry in an amount of from about 0.1% to about 1% by weight, based on the total weight of fibers present within the slurry.

20 In one embodiment, a base web of the present invention as described above can be hydraulically entangled (or hydroentangled) to provide further strength. Hydroentangled webs, which are also known as spunlace webs, refer to webs that have been subjected to
25 columnar jets of a fluid that cause the fibers in the web to entangle. Hydroentangling a web typically increases the strength of the web. Thus, according to the present invention, in order to increase the strength of a web, a base web of the present invention can be hydroentangled. For example, in a certain embodiment, the base web
30 can comprise HYDROKNIT®, a nonwoven composite fabric that contains 70% by weight pulp fibers that are hydraulically entangled into a synthetic continuous spunbonded filament material.

HYDROKNIT® material is commercially available from Kimberly-Clark Corporation of Neenah, Wisconsin. HYDROKNIT® is further disclosed in U.S. Patent No. 5,284,703 to Everhart et al. which is incorporated herein in its entirety by reference thereto.

5 In addition, the base web of the present invention can be a spunbonded, meltspun or meltblown web, or can be any other type of woven or nonwoven fabric that is absorbent to liquid water and is capable of having the anti-microbial formulation adhered thereto. In addition, the web can be a co-form material such as disclosed in U.S. Patent Nos. 4,100,324 to Anderson et al. and 5,350,624 to Georger et al., which are incorporated herein in their entireties by reference thereto.

15 In accordance with the present invention, the process of forming an anti-microbial wiper also typically involves forming an anti-microbial formulation that can be applied to the base web. A component of the anti-microbial formulation is an anti-microbial agent. The anti-microbial agent can generally include any anti-microbial compound or material that can be used as a disinfectant in wipers. Useful anti-microbial agents include silver ions, free chlorine
20 generating material, such as hypochlorites -- in particular sodium and calcium hypochlorite --, and can also include compounds that generate chlorine dioxide, such as chlorates, as well as quaternary amines -- such as alkyl aryl benzonium chloride--, halogens other than chlorine, materials such as Triclosan, and other metal ions with
25 anti-microbial activity.

 In one embodiment, where the anti-microbial agent is chlorine dioxide, the anti-microbial formulation can be a chlorine dioxide generating material containing sodium chlorate and an acid moiety. The chlorate and the acid compounds can be separated from each
30 other in the formulation, such as by supplying each of them in a coated form, where the coating releases the contents when contacted

with water, or alternatively, the two compounds could be placed in different parts of the web so that they would not come into contact with each other until the web was wetted with water. However, when a wiper containing such a formulation is contacted with water, the chlorate and the acid come into contact and chlorine dioxide is formed.

Some examples of systems that can be used to generate chlorine dioxide, for instance, are disclosed in U.S. Patent Nos. 4,681,739; 4,689,169; 5,227,168; 5,126,070; and 5,407,685, all of which are incorporated herein in their entireties by reference thereto. Another anti-microbial agent that could be employed is disclosed in U.S. Patent No. 5,837,274 to Shick *et al.*, which is also incorporated herein in its entirety by reference thereto.

As discussed above, the anti-microbial formulation of the present invention can be a particle or coating that contains an anti-microbial agent and also provides, without modification, a certain amount of controlled release characteristics for the agent. These formulations can be adhered to the base web without further modification, or they can be used with an additional polymer as part of a coating that is adhered to the base web.

In certain embodiments, a silver-zeolite complex can be utilized as the anti-microbial formulation to provide controlled release of the anti-microbial agent -- silver ions. One commercially available example of such a controlled-release silver formulation has been sold as a fabric by AgION® Technologies L.L.C. (formerly K.B. Technologies, Inc.) under the name GUARDTEX®, and is constructed from polyester and rayon and contains a silver-zeolite complex. Other suitable silver-containing anti-microbial agents are disclosed in Japanese Unexamined Patent No. JP 10/259325, which is incorporated herein by reference. Moreover, in addition to silver-zeolites, other metal-containing inorganic additives can also be used

in the present invention. Examples of such additives include, but are not limited to, copper, zinc, mercury, antimony, lead, bismuth, cadmium, chromium, thallium, or other various additives, such as disclosed in Japanese Patent No. JP 1257124 A and U.S. Patent No. 5,011,602 to Totani *et al.*, which are incorporated herein by reference. In some embodiments, the activity of the anti-microbial agent can be increased, such as described in U.S. Patent No. 5,900,383 to Davis *et al.*, which is also incorporated herein by reference.

The anti-microbial formulation can also be formed by combining an anti-microbial agent with a polymer or a mixture of polymers. Such a formulation can provide controlled release characteristics for the anti-microbial agent by controlling the properties of the polymer, and how the polymer/anti-microbial agent formulation is applied to the base web. For example, such a formulation may be simply particles of an anti-microbial agent that are mixed into a polymer prior to applying the polymer/agent mixture to the web. The polymer can then be cured or cooled to form a solid. The reduced rate of mass transfer of the agent through the solidified polymer provides the method of controlling the rate of release of the agent. Almost any form of an anti-microbial agent can be used with a polymer, including powders, microspheres, controlled-release formulations as described above, gels, liquids, or the like.

The release rate of anti-microbial agents that are a part of a polymer matrix can also be controlled by varying particle size, using polymerization chemistries, encapsulation, using porous absorbents, using soluble binders, and other similar technologies can be employed to enhance the ability to control the amount of anti-microbial agent released over a given period of time.

When an anti-microbial formulation of the present invention is formed by partially or completely coating or encapsulating an anti-microbial agent to provide further control over the release rate, any

coating known in the art to reduce the release rate of the agent can be used. For example, in one embodiment, an aqueous emulsion of an acrylic polymer may be used to coat a particulate calcium hypochlorite anti-microbial agent. In another embodiment, a microcrystalline wax coating may be employed. In yet another embodiment, polyethylene can be used. Moreover, to sufficiently reduce solubility when using a coating, it is not generally necessary to completely coat the particles. For instance, in various embodiments, a 20% acrylic polymer coating, a 33.5% acrylic polymer coating, or a 60% microcrystalline polyethylene wax coating may be used. The percentages refer to the weight of the polymer as a percentage of the weight of the anti-microbial agent. The partially coated particles would, in this case, form the anti-microbial formulation.

Various other components can be added to a formulation of the present invention to enhance control over the release rate of the anti-microbial agent. In one embodiment, for example, a polymer mixture can be added to the formulation.

A polymer mixture of the present invention can generally provide a variety of benefits. For example, the polymer mixture can enhance the strength and adhesion characteristics of the base web. Moreover, the polymer mixture can also aid in binding the anti-microbial agent to the base web, as well as enhancing the control over the release time of the anti-microbial agent. In some embodiments, the components of the polymer mixture are such that the entire mixture is capable of swelling or "blooming" when contacted with water. In some cases, such "blooming" of the polymer mixture is believed to modulate the release rate of the anti-microbial agent. As such, a polymer mixture of the present invention can generally comprise any of a variety of materials, at differing amounts, as long as the overall mixture is capable of binding the anti-microbial agent to the

base web and also modulating the release rate of the anti-microbial agent therefrom.

In this regard, one embodiment of the present invention includes a polymer mixture containing a polymer. For example, various adhesives can be used as polymers in the present invention. Examples of adhesives that can be used include, but are not limited to, acrylates, styrene butadiene, vinyl chlorides, methacrylates, acrylics (such as carboxylated acrylics), and vinyl acetates (such as self cross-linking ethyl vinyl acetate, hydrolyzed polyvinyl acetate, or non cross-linking ethyl vinyl acetate). In certain embodiments, the adhesive can comprise a carboxylated acrylic, such as a HYCAR®-brand acrylic carboxylated latex (available from B. F. Goodrich Co.).

It should be noted that although most polymers are suitable for use in accordance with the present invention, some polymers may not be suitable when used in combination with particular anti-microbial agents. For example, anionic latex adhesives may be ineffective when used in combination with certain anti-microbial agents, such as quaternary ammonium compounds, Triclosan, or silver zeolite, which are discussed in greater detail below. However, such polymers may be completely suitable when used in conjunction with other anti-microbial agents.

In some embodiments of the present invention, the polymer may also be a polymer that becomes cross-linked when dried. A cross-linked polymer can provide increased wet strength to the base web and can aid in controlling the release time of an anti-microbial agent contained within the formulation. For example, in one embodiment, a liquid latex adhesive capable of becoming cross-linked can be utilized within the polymer mixture. In this embodiment, cross-linking the latex adhesive can provide control over the water absorbency of the wiper, which can be used to effectively control the amount of the anti-microbial agent released when the wiper is

contacting by a liquid during wiping. Specifically, by reducing the amount of retained liquid after each rinse cycle, the amount of anti-microbial agent released from the wiper after each rinse cycle is also reduced. In one embodiment of the present invention, the cross-linkable adhesive can be styrene butadiene. In an alternative
5 embodiment, the adhesive can comprise a poly(ethylene vinyl acetate) copolymer.

 In some embodiments, a cross-linking agent or catalyst can be added to the polymer mixture to aid in cross-linking the polymer. By
10 varying the amount of cross-linking agent or catalyst utilized, the degree of cross-linking can vary, and thus, the control over release of the anti-microbial agent can be further enhanced. For example, in one embodiment, a poly(ethylene vinyl acetate) copolymer can be cross-linked with N-methyl acrylamide groups using an acid catalyst.
15 Suitable acid catalysts include ammonium chloride, citric acid, maleic acid, and Arizidine catalysts. The carboxylated acrylics are one example of cross-linkable adhesives.

 In general, it is often useful to add various other additives to the polymer mixture to modulate the mass transfer rate of the anti-microbial agent and, thereby, the release rate of the anti-microbial agent. For example, a polymer mixture of the present invention can also contain plasticizers to enhance the migration of the anti-microbial agent to the polymer surface such that it can be more easily removed when the wiper is wetted during use on a surface to be cleaned. One
20 suitable plasticizer includes, for example, glucose triacetate. Moreover, in some embodiments, a polymer mixture of the present can also contain various other components, such as thickeners, defoamers, water, and the like, all of which are well known additives.

 Further, other additives, such as composite particles, viscosity
30 modifiers, stabilizers, or surfactants can also be added. Composite particles can generally be added to the polymer mixture to increase

the adhesive strength of the polymer mixture without adversely interfering with the other properties of the mixture. Examples of some composite particles that can be used include clay, titanium dioxide, talc, zeolite, silica, or mixtures thereof. Moreover, as stated, one or
5 more stabilizers can be used in the polymer mixture to prevent agglomeration and to increase the stability of the suspension. Stabilizers that may be added to the polymer mixture include cellulose derivatives, such as hydroxy ethyl cellulose or methyl hydroxy cellulose. Other stabilizers that may be used include water-soluble
10 gums, acetates, such as polyvinyl acetate, and acrylics. As stated, the polymer mixture can also contain one or more surfactants. For most applications, nonionic surfactants are preferred.

Besides the above additives, a polymer mixture of the present invention can also include a visual sensor, colorant, or dye to indicate
15 when the anti-microbial agent has been partially or fully exhausted. Some examples of such a visual sensor are provided by the indicator dye described in U.S. Patent Nos. 3,704,096; 4,205,043; 4,248,597; 4,311,479; 5,317,987; and 5,699,326, all of which are incorporated herein in their entireties by reference thereto. In addition, sodium
20 thiosulfate and various blue dye mechanisms, such as those employed in the previously-mentioned WIPEX® wipes may also be employed. Furthermore, the indicator system disclosed in co-pending U.S. Provisional Application entitled "Use-Dependent Indicator System for Absorbent Articles" may be added to a bonding
25 formulation of the present invention when forming the anti-microbial wiper.

In some applications, it may also be necessary to adjust the pH of the anti-microbial agent and/or the polymer mixture before forming the formulation. In particular, one embodiment of the present
30 invention includes the addition of ammonia to both the polymer mixture and the anti-microbial agent such that the pH of each is

adjusted to a more neutral value prior to mixing. The added ammonia generally dissipates during the later step of curing, which is discussed in more detail below.

5 In general, once the polymer mixture and anti-microbial agent are incorporated into a formulation according to the present invention, the formulation can then be applied to the base web through any known method of application, such as print, print crepe, spraying, blade, saturant, coating, droplet throw, and foam applications. For example, in one embodiment, the formulation can be saturated into
10 the web, such as disclosed in U.S. Patent No. 5,486,381 to Cleveland *et al.*, which is incorporated herein by reference. Moreover, in another embodiment, the formulation can be printed onto at least one side of the base web, and, in some cases to both outer surfaces of the web. Although any method of application is suitable for use in the present invention, it should be understood that the particular
15 application method utilized can also have an affect on the release rate of the anti-microbial agent. As such, in accordance with the present invention, the method of application can also be selected as desired to further enhance the control over the release time of the anti-
20 microbial agent.

In one embodiment of the present invention, the formulation can be applied to the base web in a pre-selected pattern. For instance, the formulation can be applied to the base web in a reticular pattern, such that the pattern is interconnected forming a net-like
25 design on the surface. Moreover, the formulation can be applied according to a diamond shaped grid. The diamonds, in one embodiment, can be square having a length dimension of 1/4 inch. In an alternative embodiment, the diamonds comprising the grid can have length dimensions of 60 mm and 90 mm.

30 In an alternative embodiment, the formulation can be applied to the base web in a pattern that represents a succession of discrete

dots. This particular embodiment is generally well suited for use with lower basis weight wiping products. Applying the formulation in discrete shapes, such as dots, can provide sufficient strength to the base web without covering a substantial portion of the surface area of the web. In particular, applying the formulation to the surface of the base web can, in some instances, adversely affect the absorbency of the web. Thus, in some applications, it may be desired to minimize the amount of formulation applied.

In a further alternative embodiment, the formulation can be applied to the base web according to a reticular pattern in combination with discrete dots. For example, in one embodiment, the formulation can be applied to the base web according to a diamond shaped grid having discrete dots applied to the web within the diamond shapes.

In one embodiment of the present invention, the formulation can also be applied to one or both sides of the base web so as to cover less than 100% of the surface area of the web, particularly from about 10% to about 60% of the surface area of the web. More particularly, in most applications, the formulation will cover from about 20% to about 40% of the surface area of each side of the base web. The total amount of formulation applied to each side of the base web can range from about 2% to about 10% by weight, based upon the total weight of the base web. Thus, when the formulation is applied to each side of the web, the total add-on will be from about 4% to about 20% by weight.

According to one embodiment of the present invention, after the formulation is applied with the base web, one or both of the outer surfaces containing the formulation can then be creped by known creping processes. Although not required, creping at least one side of the base web may sufficiently disrupt the fibers within the web to increase softness, absorbency, and the bulk of the web.

In one embodiment of the present invention, the base web is first pressed into contact with a creping drum by a press roll. The formulation containing the anti-microbial agent that has already been applied to the base web causes only those portions of the web where it has been disposed to adhere to the creping surface. If desired, the creping drum can be heated for promoting attachment between the base web and the surface of the drum, as well as partially drying the base web.

Once adhered to a creping drum, the base web may then be brought into contact with a creping blade that can remove the base web from the creping drum, thereby performing a first controlled pattern crepe on the base web. In applications where the formulation is applied to each side of the base web, the web can also be creped on the second side of the web. In these applications, a second creping blade can perform a second controlled creping operation on the second side of the base web.

In one embodiment of the present invention, after the base web has been applied with the formulation and creped, if desired, the base web may then be dried and cured to form a sufficiently strong anti-microbial wiper. In one embodiment, the base web is pulled through a curing or drying station that can include any form of heating unit, such as an oven energized by infrared heat, microwave energy, hot air or the like. In addition to forming a stronger wiper, the process of curing can also aid in controlling the release time of the anti-microbial agent. Specifically, by altering the degree of polymer curing, the swelling of the polymer mixture in water can be reduced, thereby decreasing the amount of anti-microbial released from the wiper during wiping.

The wipers of the present invention may be used for any use for which a conventional absorbent wiper is used. In particular, the subject wipers are useful as hard-surface wipers where it is desirable for the wiper to have an anti-microbial effect on the surface. An

advantage of the subject wipers is that they maintain the ability to provide an anti-microbial solution after they have been rinsed in water multiple times. As mentioned above, in some embodiments, the subject wipers are suitable for use as sanitizers and/or disinfectants.

5 The present invention may be better understood with reference to the following examples.

GENERAL PROCEDURES

Method used in Examples 3 - 5 for measuring the release of anti-microbial agent from a wiper with multiple washings:

10 This method provides a simulated rinse cycle (rinse and wring out) for measuring the release of an anti-microbial agent (silver ions in this case) from a treated wiper of the present invention. Five samples were prepared of the treated wiper material (6" x 6" @ 125 grams/m² (gsm), ShopPro® hand towel). Each sample is weighed dry (as is)

15 and then individually dunked in about 700 ml of moderately hard synthetic fresh water in a 1 liter beaker. Moderately hard synthetic fresh water is 80 parts deionized water, 20 parts PERRIER® water, or equivalent, prepared as described in *Methods For Measuring The Acute Toxicity Of Effluents And Receiving Waters To Freshwater And*

20 *Marine Organisms*, EPA-600/4-90-027; C. I. Weber, Ed., pp. 32 - 35; U.S. Environmental Protection Agency, Cincinnati, OH (1991). After quickly dunking each individual sample in the water, it is removed and placed horizontally on an foraminous open mesh wire to drain for 10 min. To simulate a wringing or squeezing part of a rinse step, the five

25 samples are placed on top of one another in a clean 6 1/4" diameter Buchner funnel attached to a vacuum flask and a laboratory vacuum system. The perforated platform of the funnel is covered evenly with the samples and a flexible sheet gasket is positioned on top of the samples to form a vacuum seal to produce a uniform dewatering

30 pressure. The samples are then dewatered using laboratory vacuum for 2 minutes. The samples are then re-weighed to permit the

determination of the amount of residual wiper liquid. The fluid extracted from the five samples is collected and tested for silver content (or the content of the anti-microbial agent that is being tested). The content of anti-microbial agent in this liquid is related to the disinfecting strength or ability of the wiper.

After the first rinse and wring cycle, the samples are again individually dunked in the water solution and the steps described above are repeated. The amount of anti-microbial agent can be measured in the wash liquid after each simulated wring step. This can be repeated for as many cycles as desired.

EXAMPLE 1

An anti-microbial wiper was formed from a base web as described above. Once the web was formed, an anti-microbial agent and a polymer mixture were mixed into a formulation that could then be printed onto the web. The anti-microbial agent was an AgION™ silver-zeolite anti-microbial particle obtained from AgION™ Technologies L.L.C, West Hartford, CT. The polymer mixture included HYCAR RLP resin (available from B.F. Goodrich Specialty Chemicals, Cleveland, OH; XAMA-7 (a curing agent available from Sybron Chemicals Inc., Birmingham, NJ), CMC (as a viscosity modifier, available from Dow Chemical Co., Midland, MI), and water. The polymer mixture and anti-microbial agent were incorporated into the formulation such that the anti-microbial agent constituted 1% add-on of the wiper weight. After mixing, the formulation was then printed onto the web in accordance with the present invention.

Once applied with the formulation, the wiper was then tested to determine the amount of silver present in solution after 1, 5, 10, 15, and 20 rinses. Using atomic spectrometer measurements, it was determined that silver remained present at 140 parts per billion (ppb), 100 ppb, 90 ppb, 70 ppb, and 17 ppb, for each respective rinse.

EXAMPLE 2

The ability of an anti-microbial wiper of the present invention to effectively sustain multiple washings was demonstrated. Initially, eight wiper samples (A-H) were formed from a base web as described above. Once the web was formed, a formulation containing AgION™ silver zeolite and a polymer mixture was applied to the web. Samples A-F were applied with the formulation using either print and/or print crepe application methods, while samples G & H were applied with the formulation using a fiber saturation application method, such as described in U.S. Patent No. 5,486,381 to Cleveland *et. al.* Samples G&H contained approximately 1% silver zeolite. In addition, the characteristics of samples A-F are given below in Table 1:

Table 1: Characteristics of samples A-F.

Sample	Description	% Silver Zeolite	% Binder Solids	% Silver, dry wt.	Creping Tension
A	Air Product's LTC EVA YAY99A-973	1.0	37.90	0.050	110
B	Hycar 76208, 10% PEG (PRINT ONLY)	0.98	37.60	0.047	0
C	Hycar 2670, 10% PEG4 (PRINT ONLY)	1.85	35.90	0.093	115
D	Hycar 26706, 8% PEG 450	1.85	35.90	0.093	115
E	Hycar 26706, 10% PEG 600	0.98	37.60	0.047	105
F	Hycar 26706	1.1	35.10	0.055	92

To test the samples, each wiper sample was contacted with water for a period of ten (10) minutes. Thereafter, the samples were wrung and allowed to drip such that fluid from the wipers could be collected. The collected fluid was then tested for silver content. After collecting a fluid sample from one washing, various other washings

were then conducted. In particular, each sample was washed 20 times, with fluid samples being collected after 1, 5, 10, 15, and 20 washings as described above. The silver content remaining in each sample after 20 washing steps is given in Tables 2-9 below:

Table 2: Silver content of fluid collected (Sample A)

# of Washings	Silver Content (parts per billion)
1	210
5	99
10	70
15	270
20	81

Table 3: Silver content of fluid collected (Sample B)

# of Washings	Silver Content (parts per billion)
1	140
5	67
10	41
15	31
20	18

5

Table 4: Silver content of fluid collected (Sample C)

# of Washings	Silver Content (parts per billion)
1	140
5	130
10	46
15	37
20	29

Table 5: Silver content of fluid collected (Sample D)

# of Washings	Silver Content (parts per billion)
1	110
5	39
10	36
15	26
20	16

Table 6: Silver content of fluid collected (Sample E)

# of Washings	Silver Content (parts per billion)
1	63
5	180
10	120
15	100
20	57

5

Table 7: Silver content of fluid collected (Sample F)

# of Washings	Silver Content (parts per billion)
1	73
5	83
10	14
15	<10
20	<10

Table 8: Silver content of fluid collected (Sample G)

# of Washings	Silver Content (parts per billion)
1	180
5	100
10	<10
15	<10
20	<10

Table 9: Silver content of fluid collected (Sample H)

# of Washings	Silver Content (parts per billion)
1	150
5	75
10	<10
15	<10
20	<10

5

As indicated from Tables 2-9, an anti-microbial wiper of the present invention can controllably release an anti-microbial agent into solution, even after multiple rinsings. It should be understood, however, that a wiper of the present invention can also release an anti-microbial agent after more than 20 washings, as well as over a longer period of time.

10

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Moreover, even after 20 washing steps, an anti-microbial wiper of the present invention can continue to release a sufficient amount of anti-microbial agent to effectively kill microbes. Specifically, according to most literature, a silver content of 20 parts per billion (ppb) can effectively kill microbes, such as *E. Coli* and *Salmonella spp.* As shown in Tables 3-10, samples of the present invention can

release sufficient amounts of silver over a period of time to kill such microbes. In fact, through testing, it was determined that each sample tested above had a 99.99% kill efficacy when contacted with *E. Coli* and *Salmonella spp.* for a period of 24 hours, which is the standard exposure time set forth by the EPA.

EXAMPLE 3

This example illustrates the effect of the amount of the anti-microbial formulation and the amount of polymer binder used in the formulation on the silver content in the liquid extracted from the wiper after multiple rinses cycles.

Samples of ShopPro® hand towels (125 gsm basis weight) were treated with AgION™ silver zeolite with the use of HYCAR® #26410 Reactive Liquid Polymer resin as a polymer binder. The towels were treated by the saturation method described above in Examples 1 and 2. Three sets of towels were used and each set was treated with the amounts of silver zeolite and binder resin shown below in Table 10. After treatment, the three sets of towels were subjected to multiple rinse cycles and tested for extract silver concentration as described in the General Procedures.

Table 10: Extracted silver ion concentration after multiple rinses as a function of the initial amount of anti-microbial (AgION™), and release controlling agent (HYCAR #26410) in wipers (ShopPro®, 125 gsm) treated by saturation.

SAMPLE DESCRIPTION	NUMBER OF WASHES	SILVER CONCENTRATION IN EXTRACT (ppb)
CONTROL; 0% AgION™; 1% HYCAR®	1x	<10
	5x	<10
	10x	<10
	15x	<10
	20x	<10
1% AgION™ 1% HYCAR®	1x	140
	5x	63
	10x	29
	15x	14
	20x	17
3% AgION™ 1% HYCAR®	1x	643
	5x	205
	10x	96
	15x	75
	20x	38

5

The data of Table 10 show that the anti-microbial formulation comprising AgION™ silver zeolite and HYCAR® resin binder provided anti-microbial solutions containing silver ions after multiple rinse cycles -- at least 20 cycles, in fact. Moreover, the data showed that the level of silver ions in the retained liquid could be controlled by controlling the amount of anti-microbial agent that was initially added to the wipers.

10

15

A further set of ShopPro® towels was treated with 1% by weight AgION™ AND 0.5% by weight HYCAR® and tested for the provision of silver in the extract as described above. Here, however, the rinsing cycles were continued to 50 cycles.

Table 11: Extract silver ion concentration after multiple rinses in a wiper treated with AgION™, and HYCAR #26410 in wipers (ShopPro®, 125 gsm) treated by saturation.

SAMPLE DESCRIPTION	NUMBER OF WASHES	SILVER CONCENTRATION IN EXTRACT (ppb)
1% AgION™ 0.5% HYCAR®	1x	95
	5x	39
	10x	26
	20x	18
	30x	28
	40X	15
	50X	10

5 A wiper that was treated in the same manner as described for Table 11, was used to measure the time required for the residual liquid retained in the wiper after a rinse cycle to acquire sufficient silver ions in order to become an effective anti-microbial solution. The same technique was used for the test as described in the General
10 Procedures, except that all samples were taken after the fifth rinse cycle, and were taken at the times noted in Table 12.

Table 12: Rate of silver release into residual wiper fluid in AgION™/HYCAR® treated ShopPro fabric after five rinses.

SAMPLE DESCRIPTION	RECOVERY TIME (Min. after 5th rinse)	SILVER CONCENTRATION IN EXTRACT (ppb)
1% AgION™ 0.5% HYCAR®	0.5	36
	1	31
	2	38
	3	37

15 As the data shows, the content of the anti-microbial agent in the residual wiper fluid is quickly replenished to a level sufficient for the fluid to act as an effective disinfecting solution. In fact, such replenishment apparently occurs within the first 30 seconds after the sample is squeezed. This indicates that in normal use, the wiper

would be capable of supplying an anti-microbial solution very quickly after rinsing.

EXAMPLE 4

In this example, the effect of print treatment as compared with saturant treatment in the preparation of the subject wipers was determined as a function of the ability to continue to provide silver ions in the extract liquid after multiple rinse cycles.

ShopPro® wipers were treated with the anti-microbial formulations as described in Table 13, by either the printing method of applying the formulation, or the saturant method -- as both are described in Examples 1 and 2, above. The same amount of anti-microbial formulation (and anti-microbial agent) was used in each case. Table 13 shows the effect of the method of applying the formulation on the amount of silver that is available in the liquid extract after multiple washes.

Table 13: Extracted silver concentration after multiple rinses as a function of the method of attachment of anti-microbial agent (AgION™), and release controlling agent (HYCAR® #26410) in wipers (ShopPro® 125 gsm).

SAMPLE DESCRIPTION	NUMBER OF RINSES ^b	SILVER CONTENT OF EXTRACT (ppb) ^a
SATURANT TREATED 1% AgION™ 0.5% HYCAR®	1x	105
	5x	63
	10x	30
	20x	26
PRINT TREATED 1% AgION™ 0.5% HYCAR®	1x	250
	5x	90
	10x	89
	20x	86

Notes:

a. Aluminum content on all samples was relatively constant at <50 ppb.

b. Each rinse comprised a rinse and wring cycle as described above.

As shown in Table 13, both saturate and print treated methods of application of the anti-microbial formulation can be used to produce a product that provides continued release of anti-microbial agent at useful levels even after numerous rinses. With the same formulation, it appeared that the printing method may deliver a higher sustained level of anti-microbial agent over an extended period as compared with the saturant method. Both methods can substantially anchor the anti-microbial agent in the AgION™ formulation to the nonwoven web without significant loss of AgION™ particles during the rinse cycles. This was determined by finding that the content of released aluminum (Al is a component of the zeolite of the AgION™ formulation) in the extract did not substantially vary.

EXAMPLE 5

In this example, the effect of print treatment was compared with saturant treatment on the ability of the wiper to kill test pathogens on the wiper and in the liquid extract after multiple rinse cycles was determined.

ShopPro® wipers were treated with the anti-microbial formulations as described in Tables 14 and 15, by either the printing method of applying the formulation, or the saturant method -- as both are described in Examples 1 and 2, above. Tables 14(a) and 14(b) show the effect of the saturant method of applying the formulation on reduction of test pathogens on the wiper fabric and in the liquid extract obtained after a rinse cycle, respectively.

Table 14(a): Anti-microbial efficacy of wiper liquid extracted from AgION™/HYCAR® saturant treated nonwoven fabric wipers^b after 1, 10 and 20 rinse cycles.

NO. OF RINSE CYCLES	LIVING ORGANISMS AFTER ZERO CONTACT TIME ^a (cfu/ml)		LIVING ORGANISMS AFTER 24-HOUR CONTACT TIME (cfu/ml)		PERCENT REDUCTION (%)	
	E. coli	S. choleraesuis	E. coli	S. choleraesuis	E. coli	S. choleraesuis
1x	2.5 x 10 ⁵	1.9 x 10 ⁵	<10	<10	99.99	99.99
10x	2.6 x 10 ⁵	2.1 x 10 ⁵	<10	<10	99.99	99.99
20x	2.3 x 10 ⁵	2.3 x 10 ⁵	<10	<10	99.99	99.99

5

Notes:

a. The efficacy of the treatments was measured according to NAMSA Protocol for Assessment of Antibacterial Finishes on Textile Materials, Antimicrobial Special, Lab No. 99G 09342 00, MSMSA, NAMSA, Northwoods, OH. The anti-microbial strength of the extracts was measured by AATCC Test Method 100 using challenge organisms of *Escherichia coli* (ATCC 43895) and *Salmonella choleraesuis* (ATCC 10708).

b. ShopPro 125 gsm nonwoven wipers were treated by saturant method with 1% AgION™ and 0.5% HYCAR®.

15

Table 14(b): Anti-microbial efficacy of wiper fabric
 AgION™/HYCAR® saturant treated nonwoven fabric wipers^b after 1,
 10 and 20 rinse cycles.

NO. OF RINSE CYCLES	LIVING ORGANISMS AFTER ZERO CONTACT TIME ^a (cfu/ml)		LIVING ORGANISMS AFTER 24-HOUR CONTACT TIME (cfu/ml)		PERCENT REDUCTION (%)	
	E. coli	S. choleraesuis	E. coli	S. choleraesuis	E. coli	S. choleraesuis
1x	1.6 x 10 ⁵	1.3 x 10 ⁵	5.5 x 10 ²	4.6 x 10 ³	99.66	96.17
5x	1.5 x 10 ⁵	1.2 x 10 ⁵	1.0 x 10 ²	1.8 x 10 ⁵	99.94	NR
10x	1.5 x 10 ⁵	1.1 x 10 ⁵	6.0 x 10 ²	8.0 x 10 ²	99.61	99.27
20x	1.6 x 10 ⁵	9.4 x 10 ⁴	<1.0 x 10 ²	<1.0 x 10 ²	99.94	99.90

5

Notes:

a. The efficacy of the treatments was measured according to
 NAMSA Protocol for Assessment of Antibacterial Finishes on Textile
 Materials, Antimicrobial Special, Lab No. 99G 09342 00, MSMSA,
 NAMSA, Northwoods, OH. The anti-microbial strength of the extracts
 was measured by AATCC Test Method 100(modified) using challenge
 organisms of *Escherichia coli* (ATCC 43895) and *Salmonella*
choleraesuis (ATCC 10708).

b. ShopPro 125 gsm nonwoven wipers were treated by
 saturant method with 1% AgION™ and 0.5% HYCAR®.

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Tables 15(a) and 15(b) show the effect of the printing method of applying the formulation on reduction of test pathogens on the wiper fabric and in the liquid extract obtained after a rinse cycle, respectively.

- 5 Table 15(a): Anti-microbial efficacy of wiper liquid extracted from AglON™/HYCAR® printing treated nonwoven fabric wipers^b after 1, 10 and 20 rinse cycles.

NO. OF RINSE CYCLES	LIVING ORGANISMS AFTER ZERO CONTACT TIME ^a (cfu/ml)		LIVING ORGANISMS AFTER 24-HOUR CONTACT TIME (cfu/ml)		PERCENT REDUCTION (%)	
	E. coli	S. choleraesuis	E. coli	S. choleraesuis	E. coli	S. choleraesuis
1x	2.2 x 10 ⁵	1.3 x 10 ⁵	<10	<10	99.99	99.99
10x	2.9 x 10 ⁵	1.1 x 10 ⁵	<10	<10	99.99	99.99
20x	2.0 x 10 ⁵	1.3 x 10 ⁵	<10	<10	99.99	99.99

Notes:

- 10 a. The efficacy of the treatments was measured according to NAMSA Protocol for Assessment of Antibacterial Finishes on Textile Materials, Antimicrobial Special, Lab No. 99G 09342 00, MSMSA, NAMSA, Northwoods, OH. The anti-microbial strength of the extracts was measured by AATCC Test Method 100 using challenge
- 15 organisms of *Escherichia coli* (ATCC 43895) and *Salmonella choleraesuis* (ATCC 10708).

 b. ShopPro 125 gsm nonwoven wipers were treated by printing method with 1% AglON™ and 0.5% HYCAR®.

Table 15(b): Anti-microbial efficacy of wiper fabric
 AglON™/HYCAR® printing treated nonwoven fabric wipers^b after 1,
 10 and 20 rinse cycles.

NO. OF RINSE CYCLE	LIVING ORGANISMS AFTER ZERO CONTACT TIME ^a (cfu/ml)		LIVING ORGANISMS AFTER 24-HOUR CONTACT TIME (cfu/ml)		PERCENT REDUCTION (%)	
	E. coli	S. choleraesuis	E. coli	S. choleraesuis	E. coli	S. choleraesuis
1x	1.3 x 10 ⁵	1.6 x 10 ⁵	<1.0 x 10 ²	3.0 x 10 ²	99.93	99.83
5x	1.4 x 10 ⁵	1.9 x 10 ⁵	<1.0 x 10 ²	<1.0 x 10 ²	99.93	99.95
10x	1.3 x 10 ⁵	1.6 x 10 ⁵	<1.0 x 10 ²	1.0 x 10 ³	99.93	99.86
20x	1.5 x 10 ⁵	1.7 x 10 ⁵	<1.0 x 10 ²	<1.0 x 10 ²	99.93	99.94

5

Notes:

a. The efficacy of the treatments was measured according to
 NAMSA Protocol for Assessment of Antibacterial Finishes on Textile
 Materials, Antimicrobial Special, Lab No. 99G 09342 00, MSMSA,
 10 NAMSA, Northwoods, OH. The anti-microbial strength of the extracts
 was measured by AATCC Test Method 100(modified) using challenge
 organisms of *Escherichia coli* (ATCC 43895) and *Salmonella*
choleraesuis (ATCC 10708).

b. ShopPro 125 gsm nonwoven wipers were treated by printing
 15 method with 1% AglON™ and 0.5% HYCAR®.

It was shown that either the saturant treated or the printing
 treated wipers provided liquid extract after 20 rinse cycles that was
 capable of obtaining a 99.99% kill on both *E. coli* and *S. choleraesuis*
 test pathogens. Accordingly, it is believed that either of these
 20 methods is capable of providing effective anti-microbial wipers of the
 present invention.

In the measurements of the retardation of cell growth on the wiper fabric itself, neither method of treatment provided as complete a reduction as did the liquid effluents -- although a reduction of at least 99% was obtained in most cases. It is possible that this indicates a less effective contact of the wiper surface (and the anti-microbial agent) with the microorganisms that were applied to the surface. This could indicate that the surface of the wiper could be less irritating to the skin of the user when more aggressive anti-microbial agents are employed.

EXAMPLE 6

Another exemplary wiper product was produced by flexogravure printing a Hydroknit® material (125 gsm) with a blue ink having an overall shell pattern to provide a total AgION™ add-on of 0.20% (based on weight of the AgION™ anti-microbial per weight of wiper material). The ink consisted of a mixture of cross-linkable acrylic, AgION™ silver-zeolite complex, blue pigment (Graphtol 6825, available from Clariant), and various ink modifiers as set forth below:

Table 16: Exemplary Anti-Microbial Wiper Formulation

COMPONENT	% ACTIVE	% AMOUNT BY WEIGHT
Hydroknit® (125 gsm)		
AgION™ anti-microbial silver zeolite complex	20	48.6
Hycar 26684	50	19.4
Xama-7	100	0.3
Graphtol 6825	20	1.4
Ammonium hydroxide	27	1.0
Water		29.3

Although various embodiments of the invention have been described using specific terms, devices, and methods, such description is for illustrative purposes only. The words used are words of description rather than of limitation. It is to be understood that changes and variations may be made by

those of ordinary skill in the art without departing from the spirit or scope of the present invention, which is set forth in the following claims. In addition, it should be understood that aspects of the various embodiments may be interchanged both
5 in whole or in part. Therefore, the spirit and scope of the appended claims should not be limited to the description of the preferred versions contained therein.

WHAT IS CLAIMED IS:

1. A method of forming an anti-microbial wiper capable of providing liquid anti-microbial solution after multiple rinse cycles, the method comprising the steps of:
 - 5 providing a controlled release anti-microbial formulation comprising an anti-microbial agent; and
 - adhering said formulation to an absorbent web containing fibers, which web retains liquid after each rinse cycle, and which formulation releases sufficient anti-microbial agent into the retained liquid after each of at least five normal rinse cycles so that the
10 retained liquid is an anti-microbial solution.
2. A method as defined in claim 1, wherein said anti-microbial formulation comprises a polymer or a polymer mixture.
3. A method as defined in claim 2, wherein said polymer
15 mixture comprises a water-swellaable polymer such that the degree of swelling of said water-swellaable polymer at least partially controls said release of said anti-microbial agent.
4. A method as defined in claim 2, wherein said polymer comprises a latex adhesive.
- 20 5. A method as defined in claim 4, wherein said latex adhesive is capable of becoming cross-linked.
6. A method as defined in claim 1, wherein said anti-microbial formulation comprises a source of anti-microbial metal ions.
7. A method as defined in claim 6, wherein said anti-
25 microbial formulation comprises a source of ions of a metal selected from the group consisting of silver, copper, zinc, mercury, antimony, lead, bismuth, cadmium, chromium and thallium.
8. A method as defined in claim 7, wherein said metal comprises silver.
- 30 9. A method as defined in claim 1, wherein said anti-microbial formulation comprises a source of free chlorine.

10. A method as defined in claim 1, wherein said anti-microbial formulation comprises calcium hypochlorite particles.

11. A method as defined in claim 1, wherein said anti-microbial formulation comprises a quaternary ammonium compound.

5 12. A method as defined in claim 11, wherein said quaternary ammonium compound comprises alkyl aryl benzonium chloride.

10 13. A method as defined in claim 2, wherein said polymer or polymer mixture further comprises an additive selected from the group consisting of a cross-linking agent, a catalyst, a thickener, a plasticizer, a defoamer, a colorant, a visual sensor, a pigment, composite particles, a viscosity modifier, a stabilizer, a surfactant, and combinations thereof.

15 14. A method as defined in claim 1, wherein the adhering of said anti-microbial formulation comprises spraying the formulation onto said web.

20 15. A method as defined in claim 1, wherein the adhering of said formulation onto said web comprises a process chosen from the group consisting of printing, blade applying, coating, droplet throwing, print creping, saturating, and foam applying.

16. A method as defined in claim 1, wherein said web has at least two surfaces, said formulation being applied to said at least one of said two surfaces of said web in a pre-selected pattern.

25 17. A method as defined in claim 16, wherein said formulation covers from about 10% to about 60% of said at least one surface of said web.

18. A method as defined in claim 1, wherein said formulation covers from about 20% to about 40% of said at least one surface of said web.

19. A method as defined in claim 16, wherein said formulation covers from about 10% to about 60% of both surfaces of said web.

5 20. A method as defined in claim 2, further comprising the step of curing said polymer mixture after said formulation has been applied to said web.

21. A method as defined in claim 16, further comprising the step of creping said at least one surface of said web to soften said web after said formulation has been applied to said web.

10 22. A method as defined in claim 1, wherein said fibers of said web comprise pulp fibers.

23. A method as defined in claim 1, wherein said fibers of said web comprise synthetic fibers.

15 24. A method of forming an anti-microbial wiper for disinfecting hard surfaces comprising the steps of:
providing a cloth-like absorbent base web containing fibers and capable of retaining liquid after a rinse cycle, said web having two outer surfaces; and

20 adhering an anti-microbial formulation to said web, said formulation comprising an anti-microbial agent and a polymer, said anti-microbial formulation containing an anti-microbial agent being capable of activation when said web is contacted with a liquid, said activation including the release of a portion of said anti-microbial agent into the retained liquid to form an anti-microbial solution, said
25 polymer being capable of controlling the rate of release of the anti-microbial agent from the anti-microbial formulation so that said anti-microbial solution is formed after at least five rinse cycles.

30 25. A method as defined in claim 24, wherein said polymer comprises an additive selected from the group consisting of a cross-linking agent, a catalyst, a thickener, a plasticizer, a defoamer, a

colorant, a visual sensor, a pigment, composite particles, a viscosity modifier, a stabilizer, a surfactant, and combinations thereof.

26. A wiper capable of providing liquid anti-microbial solution after numerous rinse cycles comprising:

5 a controlled release anti-microbial formulation comprising an anti-microbial agent, which formulation is adhered to an absorbent, cloth-like web which retains liquid after each rinse cycle,

10 which formulation releases sufficient anti-microbial agent into the retained liquid after each of at least five normal rinse cycles so that the retained liquid is an anti-microbial solution.

27. A wiper as defined in claim 26, wherein said anti-microbial formulation comprises an antimicrobial agent and a polymer.

15 28. A wiper as defined in claim 27, wherein said polymer comprises a latex adhesive.

29. A wiper as defined in claim 28, wherein said latex adhesive is capable of becoming cross-linked.

20 30. A wiper as defined in claim 26, wherein said anti-microbial agent comprises a source of metal ions where the metal is selected from the group consisting of silver, copper, zinc, mercury, antimony, lead, bismuth, cadmium, chromium and thallium.

31. A wiper as defined in claim 30, wherein said metal comprises silver.

25 32. A wiper as defined in claim 26, wherein said anti-microbial formulation comprises a source of free chlorine.

33. A wiper as defined in claim 26 wherein said anti-microbial formulation comprises a source of chlorine dioxide.

34. A wiper as defined in claim 32 wherein said anti-microbial formulation comprises calcium hypochlorite particles.

30 35. A wiper as defined in claim 26, wherein said anti-microbial formulation comprises a quaternary ammonium compound.

36. A wiper as defined in claim 28, wherein said quaternary ammonium compound comprises alkyl aryl benzonium chloride.

5 37. A wiper as defined in claim 27, wherein said polymer further comprises an additive selected from the group consisting of a cross-linking agent, a catalyst, a thickener, a plasticizer, a defoamer, a colorant, a visual sensor, a pigment, composite particles, a viscosity modifier, a stabilizer, a surfactant, and combinations thereof.

10 38. A wiper as defined in claim 26, wherein said formulation covers from about 10% to about 60% of said at least one surface of said web.

39. A wiper as defined in claim 26, wherein said formulation covers from about 20% to about 40% of said at least one surface of said web.

15 40. A wiper as defined in claim 26, wherein said formulation covers from about 10% to about 60% of both surfaces of said web.

41. A wiper as defined in claim 26, wherein said fibers of said web comprise pulp fibers.

42. A wiper as defined in claim 26, wherein said fibers of said web comprise synthetic fibers.